

Effect of Electrolyte pH on Phosphate Adsorption by Soils

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Effect of pH on phosphate adsorption by different soils was studied by varying the pH of supporting electrolytes NaCl and CaCl₂. Variation in pH of NaCl did not markedly affect phosphate adsorption in all the soils. On the other hand, it decreased with pH from 4 to 6 and abruptly increased above pH 7.0 when CaCl₂ was used as supporting electrolyte.

INTRODUCTION

Phosphate adsorption by soils has been reported¹⁻⁵ to be influenced by several factors such as pH, nature of cations and ionic strength of soil solution, organic matter content and Fe and Al oxides. Among these factors, the effect of pH is least understood⁶. There have been conflicting reports about the effect of pH on phosphate adsorption by soils. Some workers⁷ have shown that phosphate adsorption decreased with increase in pH from 3 to 8, while others⁸ have shown that phosphate adsorption increased with increase in pH or was unaffected by changes in soil pH at low P additions⁹.

It has been found¹⁰ that phosphate adsorption increases with increase in ionic strength of supporting electrolyte. With same concentration of supporting electrolyte, phosphate adsorption is greater in CaCl₂ solution as compared to NaCl solution. Amount of phosphate once adsorbed undergoes desorption to maintain the dynamic equilibrium. Phosphate per cent desorption decreases with increase in ionic strength and is greater in NaCl solution as compared to CaCl₂ solution of same strength. In the present investigation, effect of pH on phosphate adsorption by soils has been studied by varying the pH of supporting electrolytes NaCl and CaCl₂.

EXPERIMENTAL

Ten surface soil samples from bench-mark soils of Punjab representing Gahri Bhagi, Jassi Pauwali, Jodhpur Ramana (from arid region), Fatehpur, Kanjli, Ladowal, Nabha, Sadhu (from semiarid region), Chamror and Dhar (from humid region) soil series were used in the present investigation. The soil samples after drying in air were crushed and passed through 2 mm sieve. The samples were stored in sealed glass containers. The characteristics of the soil samples are given in Table-1.

Solutions containing 161 μ Mole P/litre and 322 μ mole-P/litre were prepared by dissolving KH₂PO₄ in 0.01 M NaCl and 0.01 M CaCl₂ solutions. In the soil testing programme the soils containing less than 5 μ g P/g soils are classified as deficient in phosphorus and this concentration corresponds with 161 μ mole P/litre. The other concentration of 322 μ mole P/litre corresponds with 10 μ g P/g soil (which is near the sufficiency level of 9 μ g P/g soil). The pH of electrolyte

solution varied from 4.0 to 9.0 using acetic acid and sodium hydroxide. The soil sample (1 g) was equilibrated with 50 mL of the respective P solution in reagent bottles using a soil : solution ratio of 1 : 50. The diffusion of ions at the solid-solution interface is not the rate limiting step. In a kinetic study, it was found that equilibrium was established after 33 h. So sealed reagent bottles were incubated at 25°C for 48 h with frequent shaking. These soil electrolyte suspensions were then centrifuged at 3000 rpm and the concentration of P in the reagent was determined spectrophotometrically at wavelength 760 nm using ascorbic acid method¹⁵.

TABLE-I
CHARACTERISTICS OF SOILS

Soil	ubgroup	%			pH	EC dsm ⁻¹	OC g kg ⁻¹	CaCO ₃ g kg ⁻¹	CBC C mol kg ⁻¹
		Sand	Silt	Clay					
Gabri	Ustochreptic	53.6	27.8	18.6	7.9	0.25	2.2	6.0	7.8
Bhagi	camborthid								
Jassi	Ustic	80.9	14.1	5.0	8.2	0.19	0.9	22.0	6.1
Pauwali	torripsamment								
Jodhpur	Ustochreptic	72.5	18.5	9.0	8.1	0.18	0.9	30.0	5.6
Ramana	camborthid								
Fathepur	Typic ustipamment	92.4	4.1	8.5	7.8	0.21	1.2	1.0	2.8
Kanjli	Typic ustochrept	44.5	37.3	18.4	8.5	0.24	4.0	10.0	10.1
Nabha	Typic ustochrept	38.9	42.7	19.0	8.0	0.18	4.3	2.0	11.1
Ladhowal	Typic ustifluent	19.4	63.6	17.0	8.2	0.21	5.4	19.0	13.4
Sadhu	Vertic ustochrept	5.4	34.9	59.7	8.2	0.27	7.1	7.7	30.4
Chamror	Dysritic eutrochrept	42.0	43.4	14.6	7.0	0.20	9.1	—	11.7
Dhar	Typic eutrochrept	34.6	48.6	16.8	7.6	0.30	5.8	4.0	10.8

RESULTS AND DISCUSSION

The adsorption of phosphate by soils from electrolyte solutions (0.01 M NaCl and 0.01 M CaCl₂) varying in pH (4–9) at two different concentrations of P (161 μmole/litre) is plotted in Figs. 1–4. A perusal of these data indicates that pH did not markedly affect phosphate adsorption when sodium chloride was used as a supporting electrolyte up to pH 8.0. Above this pH, phosphate adsorption either slightly increased or remained constant. This may be due to the fact that at these P concentrations, the number of phosphate ions sorbed is low and these ions are sorbed mainly at the high affinity sites¹¹ with little or no repulsive forces from the adjacent phosphate ions on the surface. Therefore, these ions cannot be replaced by the increasing concentration of OH⁻ ions under conditions of increasing pH, not are they affected by the increasing repulsive forces between the increased surface negative charge and phosphate anions as pH rises.

Variation in pH of calcium chloride solution affected phosphate adsorption in a different manner at the two P concentrations (Figs. 1–4). At low P concentration (161 μmole/litre) phosphate adsorption increased in almost all the soils. At high

P concentration (322 $\mu\text{mole/litre}$), there was an abrupt increase in phosphate adsorption pH 8.0 suggesting that concentration of P plays a significant role when CaCl_2 is used as a supporting electrolyte. The decrease in phosphate adsorption with increase in pH was due to the increased concentration of hydroxyl ions as pH increased and resulted in greater competition of these ions with phosphate ions for sorption. Increase in phosphate adsorption above pH 7.0 was due to adsorption of Ca^{2+} ions on hydrous oxide and kaolinite surfaces, by forming basic calcium phosphate especially at high concentration of calcium. These soils contain about 10–15 per cent kaolinite and appreciable amounts of dithionite-citrate-bicarbonate extractable hydrous oxides of Fe and Mn.

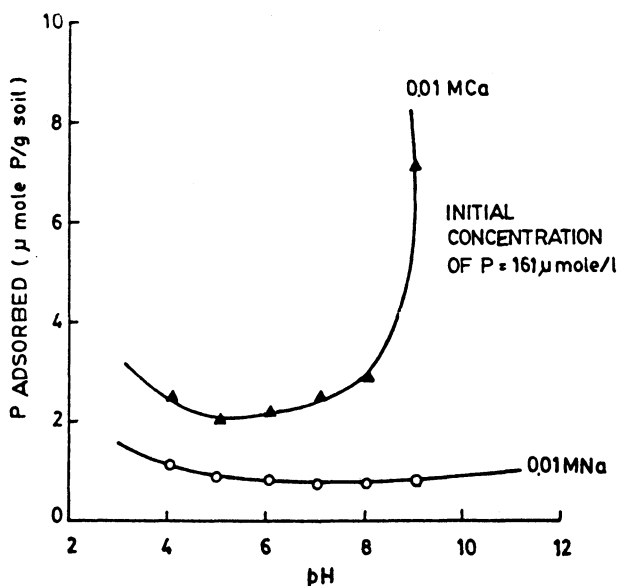


Fig. 1. Effect of pH of supporting electrolyte solution on phosphate adsorption by Gahri Bhagi soil at 25°C.

It is clear from Figs. 1–4 that phosphate adsorption is also affected by the cationic species in the electrolyte. Phosphate adsorption was greater in calcium chloride as compared to sodium chloride solution at a particular pH. The higher amounts of phosphate adsorption in the presence of Ca^{2+} ions may be due to formation of surface complex between Ca^{2+} and phosphate ions^{13,14}. Helyer *et al.*¹² proposed a model where Ca^{2+} ion fits in the cavity between two adjacent phosphate ion. Thus reducing the electrostatic repulsion between the negatively charged ions, thereby facilitating greater adsorption of phosphate ions.

The findings of this investigation have practical implications for the use of phosphate fertilizers. When these fertilizers are applied to soils, these undergo dissolution to form phosphate ions in soil solution. If Ca^{2+} is the dominant cation in soil (as in case of calcareous soils), there will be greater adsorption of phosphate ions as compared with soils containing high amount of Na^+ ions. As soil solution is depleted of phosphate ions due to plant uptake or leaching, the

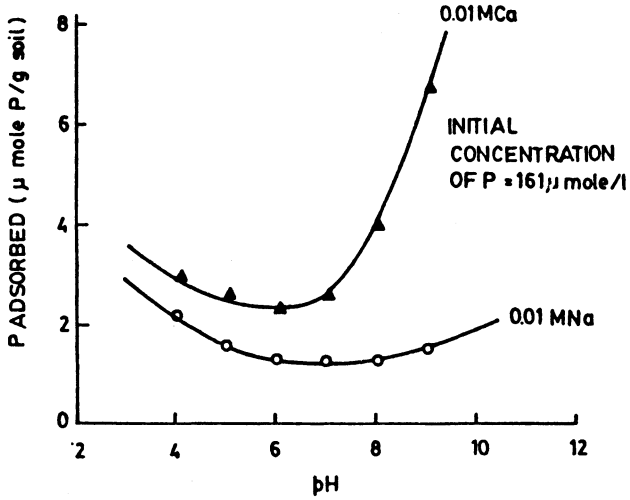


Fig. 2. Effect of pH of supporting electrolyte solution on phosphate adsorption by Kanjli soil at 25°C

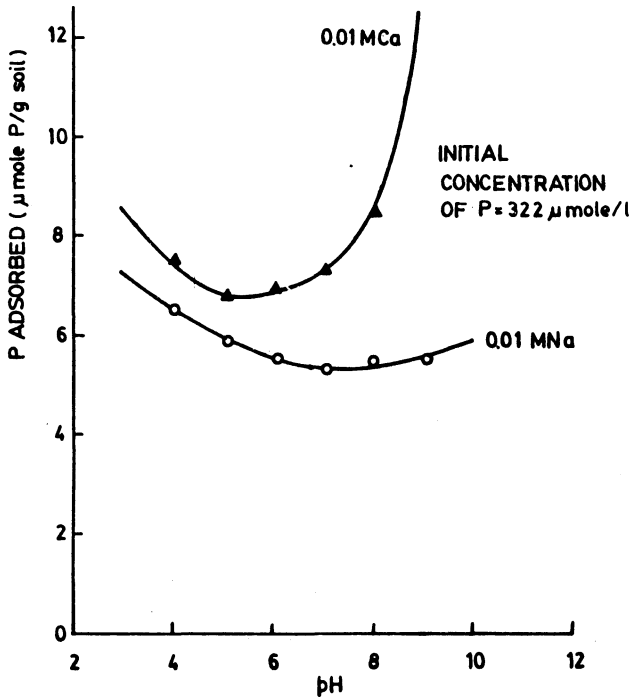


Fig. 3. Effect of pH of supporting electrolyte solution on phosphate adsorption by Dhar soil at 25°C.

adsorbed phosphates are desorbed. Our preliminary studies have shown that phosphate desorption decreases with increase in ionic strength and is greater in NaCl solution as compared to CaCl₂ solution at a particular ionic strength. Thus

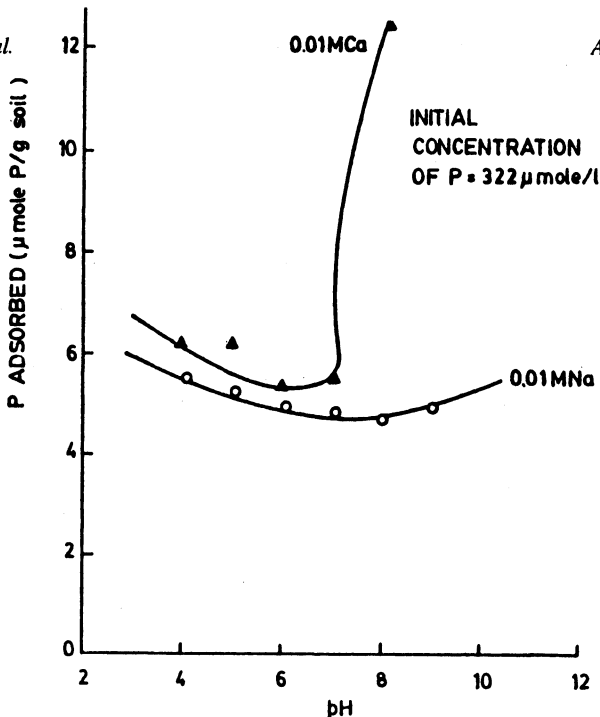


Fig. 4. Effect of pH of supporting electrolyte solution on phosphate adsorption by Chamror soil at 25°C.

the use efficiency of phosphate fertilizers is likely to be low in soils rich in calcium due to higher adsorption and lower desorption compared with soils rich in sodium. Generally, sodium is predominant in saline/alkali soils whereas calcium predominates in soils of arid/semi-arid regions.

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